

A METHOD FOR CONTROLLING THE MOLECULAR WEIGHT AND FLUIDITY OF POLYMERS

FIELD OF THE INVENTION

001. This invention pertains to processes for controlling the molecular weight and fluidity of polymer melts by incorporating into the solid polymer, materials in the form of gases, liquids, mists, and their blends. The invention also pertains to the products made thereby.

BACKGROUND

002. Polymers are made up of long chain molecules, i.e. macromolecules, which entangle themselves. The entanglement provides mechanical strength to the polymer in the solid and melt phases, but also increases the viscosity of the melt phase. Higher polymer chain molecular weight in general results in higher viscosity, and therefore a higher power requirement for processing a given polymer at a given temperature.

003. Control of molecular weight, and hence the viscosity and solid phase physical properties of a polymer, has long been a goal of many processors. Polymer chains can be lengthened by the addition of cross linking agents, or by post polymerization in the melt phase of a reactor made prepolymer. This technology is described and exemplified in patent U.S. 6,657,039 to LG Chemical, in which polycarbonate is subjected to a treatment like this.

004. An approach to molecular weight reduction that has become common is the controlled degradation of the polymer chains using a chain breaking agent. Peroxides are commonly used for this purpose, and U.S. 5,530,073 to Amoco describes the use of 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane with polypropylene. Another example is U.S. 6,620,892 to Atofina in which is disclosed a process for production of a controlled-rheology resin, the process comprising adding at least one stable free radical to a resin containing a propylene homopolymer or copolymer, whereby said process increase the fluidity index of the resin by cuts of the chains, and a solid product

that has an increased fluidity index is formed. Other references in the patent art to this technology include WO-A-96/12753; EP-A-570 812; U.S. 5,932,660; JP-A-07/138 320; U.S. 5,530,073; WO-A-96/06872; U.S. 5,705,568; U.S. 3,862,265; U.S. 5,945,492; CA-A-2 258 305; U.S. 4,900,781; DE-A-1 694 563; U.S. 4,672,088; and EP-A-0 853 090.

005. There are many other examples in the prior art of this approach with polyolefins, for a recent review see for example D. Munteanu, in "Plastics Additives, 5th Edition, ed. H. Zweifel, chapter 14, Hanser Publishers, Munich.

006. A major limitation of this approach to controlling the molecular weight of polymers is that molecular weight and fluidity, as measured by viscosity, are linked, and the benefits obtained by changing one can be offset by the disadvantages caused by the change that necessarily takes place in the other. For example, superior physical properties in the solid phase as obtained from higher molecular weight, are offset by higher processing costs due to higher power requirements.

007. Some of these disadvantages are overcome in US Patents 5,885,495 and 6,210,030 issued to the present inventor, respectively describe a process and an apparatus capable of controlling the viscosity of polymeric materials by disentanglement of the molecular chains of which the polymer is comprised. In addition to these patents, the present inventor has now found that it is possible to further control the viscosity and molecular weight of polymers by incorporating additives into the polymer in the solid phase, in such a way that the additives have been permeated into the polymer and become in intimate contact with the polymer chains. Some of the additives would be expected to be inert with respect to the chemical structure of the chains still have the desired effect.

008. In addition, the present inventor has discovered that polymer chains that have been subjected to the process of the invention have fluidity and molecular weight properties that indicate that they are disentangled, and have a degree of disentanglement greater than zero.

009. In an embodiment of the present invention, pellets of polymers are inoculated with a dosed amount of chemical molecules and are subjected to the

heat and shear of a melt processing operation thus modifying the molecular weight distribution, viscosity and degree of disentanglement of the polymer.

BRIEF SUMMARY OF THE INVENTION

0010. The present invention provides a process to incorporate into polymeric materials at a temperature below the solidification temperature of the polymer, and preferably when the resin is still in the form of pellets or granules, and under controlled conditions of temperature and pressure, amounts of other molecules ("the permeating material" or "permeant") whose presence inside the polymer is able to affect its future behavior and properties.

0011. The physical form of the material to be inserted into the free volume of the polymer can be a simple gas, a vapor, a fluidized bed or an aerosol or a mixture of any of these. The material can also be in the form of a liquid from which molecules can diffuse, such as a mist or a bulk liquid, or an emulsion. The material can also be in the form of a solid, preferably a finely divided solid, in which molecules diffuse from a solid that is in contact with the polymer surface. Examples of solid phase materials are bulk materials, or particles in suspension, including nanoparticles,

0012. After controlled exposure to the permeating material, and return to storage conditions, generally room temperature and atmospheric pressure, the free volume of the polymer is now occupied with molecules from that substance, and their presence in the structure may result in a modification of the polymer characteristics, either in the solid state, or in the molten state.

BRIEF DESCRIPTION OF THE FIGURES

0013. In figure 1 is shown a schematic diagram of an apparatus that can carry out the process of the present invention in that a supply of polymer pellets is dosed with a permeant before being melt processed.

0014. In figure 2 is shown a design for a manifold of which the equipment of figure 1 comprises.

0015. In figure 3 is shown a design for a dosing chamber suitable for use in the process of the present invention.

0016. In figure 4 is shown a further embodiment of the invention, in which product from a polymerization reactor is extruded, pelletized, and then dosed with permeant.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

0017. The invention can be best understood by reference to the following definitions.

0018. By “polymer chain” is meant the molecular backbone of the polymer. In a linear polymer, the backbone comprises the longest sequence of connected atoms in any given molecule. In a highly branched polymer such as low density polyethylene (LDPE), the backbone comprises all of the carbon atoms in a given molecule.

0019. The terms “polymer” and “polymeric material” as used herein are synonymous, and are defined as in the Handbook of Chemistry and Physics, 84th Edition CRC Press, 2003-2004, page 13-7 to 13-14, which pages are hereby incorporated herein by reference.

0020. The term “disentangled” as used in the context of polymers, refers to polymer pellets or products produced by “disentanglement”, which refers to the process of either partially or completely removing entanglements among polymer chains in a given polymer sample. Both US 5,885,495 and US 6,210,030, and both to Ibar and both incorporated herein by reference in their entirety, disclose use of disentanglement to control, and essentially lower, the viscosity on a polymer melt. These patents also disclose the disentanglement processing window parameters which optimize the efficiency of the viscosity control invention.

0021. The preferred means for disentangling uses the “Tek Flow Processor”, which refers to a commercial apparatus of the embodiment of the invention of U.S. 6,210,030 in which the viscosity of a polymer is controlled by disentanglement of the polymer chains that the polymer comprises. The Tek Flow Processor is available from Stratek Plastic Ltd. (Dublin, Ireland).

0022. By "drying" is meant the process by which heat and, optionally vacuum, to remove moisture from a polymer. An example apparatus combining heat and vacuum means to remove water molecules from a polymer pellet or product is commercially available from the Maguire Corporation (Pennsylvania, USA), however, many commercial driers in many configurations are available to, and would be known by, one skilled in the art. It is to be understood that the dried polymer that is obtained from a drying step does not necessarily have zero moisture content, but rather is to be understood as having sufficient moisture that the polymer can be passed to the subsequent processing steps of the invention, with whatever residual moisture in the sample not causing any loss in efficacy of the process.

0023. By "permeant" is meant a substance that enters the free volume of a solid polymer. The permeant can be in the form of a liquid, gas, plasma or solid.

0024. The term "gas mixture" refers to the product obtained by mixing two or more gases or volatiles in a chamber, at a temperature, pressure and under concentration conditions which allow the mixture to be transferable to a vacuum chamber holding the pellets or the parts to be treated according to the present invention. For instance, gas mixture can combine an inert gas and a chemical volatile, in a given proportion. The gas may be ionized or one of its components may be ionized by plasma or high voltage discharge.

0025. The term "plasma" refers to the state of matter obtained by subjecting a gas to an electrical discharge. A plasma generally comprises species such as ions and atoms that are not generally available in states of matter that are available outside of the discharge.

0026. By "temperature of solidification" is meant that temperature of a polymer, copolymer or polymer blend, below which the material presents the mechanical characteristics of a solid.

0027. By "polymer pellets" is meant the resin products usually produced in reactors, and stocked in bags at room temperature, or a temperature below their temperature of solidification, under either pellets, granular, chips or powder (fluff) form.

0028. By “means for forming” is meant a process by which a polymer melt is turned into a useful article. Forming means are well known to those skilled in the art and include, but are not limited to for the purposes of this disclosure, injection molding, blow molding, film extrusion, sheet extrusion, extrusion to form tapes or fibers, or tubes, and rotomolding.

0029. The “% chain scission” of a polymer sample is defined herein with respect to a reference material by the formula;

$$0030. \% \text{ chain scission} = 100 (1 - M_w / M_{wref})$$

0031. where M_w is the weight average molecular weight of the polymer sample, and M_{wref} is the weight average molecular weight of a control sample, normally the polymer chains before scission.

0032. The “degree of disentanglement” is a measure of the change in melt flow index (MFI) of a virgin, or disentangled resin upon being subjected to a process of the invention, corrected for any change in molecular weight that the polymer chains may have undergone.

0033. The formula for degree of disentanglement is given by:

$$\text{Degree of Disentanglement} = 100 \left[\frac{MFI_{final}}{MFI_{initial} \left(\frac{M_{w_{initial}}}{M_{w_{final}}} \right)^{3.4}} - 1 \right]$$

0034. For example, if a virgin polymer of MFI = 10.0 and Mw of 25,000 is subjected to the process of the invention and is transformed to a MFI of 250 and a Mw of 22,000. The degree of disentanglement of the final polymer is then;

$$\begin{aligned} & 100 \times [(250/15.44) - 1] \\ & = 1519\% \end{aligned}$$

0035. A virgin resin therefore, by definition, has a degree of disentanglement of zero. The term “essentially zero” as used herein when referring to degree of disentanglement refers to zero within the experimental error of the MFI and M_w measurement. However, a resin that has been

aminopheonols, thioethers, phosphates and phosphonites and sterically hindered amine. Also metal deactivators, amides of aliphatic and aromatic mono and dicarboxylic acids and their N-monosubstituted derivatives such as for example N,N' diphenyl oxamide,

0039. Also permeants such as cyclic amides such as barbituric acid, hydrazones and bishydrazones of aliphatic and aromatic aldehydes, as benzaldehyde and salicylaldehyde or of o-hydroxy-aryl-ketones. Also, bis acylated hydrazine derivatives, heterocyclic compounds, for example melamine, benzotriazoles, 8-oxyquinoline, hydrazones and acylated derivatives of hydrazinotriazines, aminotriazoles and acylated derivatives thereof.

0040. Also polyhydrazides, molecular combinations of sterically hindered phenols and metal complexing groups, nickel salts of benzyl phosphonic acids, alone, or in combination with other antioxidants or metal deactivators, pyridenethiol tin compounds and phosphorous acid esters of a thiobisphenol.

0041. Solvents for the specific polymer system can also be used. When used herein, a solvent for the polymer is as defined in the Handbook of Chemistry and Physics, 84th Edition CRC Press, 2003-2004, page 13-6, which is hereby incorporated herein by reference. For example, toluene, xylene, halogenated benzenes such as dichloro- and trichlorobenzene can be used for polyolefins.

0042. Suitable permeants for use in the invention are also chlorofluorocarbons as described in the Handbook of Chemistry and Physics, 84th Edition CRC Press, 2003-2004, page 6-144 to 6-146, which pages are hereby incorporated herein by reference.

0043. The scope and claims of the invention are not, however, intended to be limited by the above list, and any permeant that is effective in modifying the molecular weight of the polymer is suitable for use in the invention.

0044. The method of the invention can be further understood by reference to the figures. In figure 1 is shown a schematic diagram of an embodiment of the process of the invention in which disentangled polymer pellets are supplied from a Gaylord container (10) via a vacuum hose to a loading device (11). In a typical

embodiment, the loading device will be a gravimetric feeder, as supplied for example by K-Tron (of Pitman, NJ), that supplies pellets at a controlled rate or in controlled batch weights to the downstream process.

0045. Referring again to figure 1, the pellets are then supplied to a heating chamber (12) where they are heated to a temperature suitable to the polymer plus permeant system being treated. From the heating chamber the pellets are supplied to a vacuum chamber (13), which is evacuated to a pressure of 0.1bar or less, more preferably 10^{-2} bar or less, and most preferably 10^{-3} Torr or less. From the vacuum chamber, the pellets are passed to a doping chamber (14), where they are exposed to the permeant which is supplied via a manifold (15). From the manifold, the pellets are fed to a metering device (16) that directly feeds them to the throat of an extruder (17).

0046. In a preferred embodiment of the process, the processes corresponding to steps 12, 13, and 14 in figure 1 are carried out in one container, which is one of at least a pair of containers and preferably three containers, which are indexed around a carousel. A piece of equipment of this type is manufactured by Maguire Products (Aston, PA).

0047. The Maguire dryer operates with 3 Stainless Steel canisters that are mounted directly onto a carousel that indexes counterclockwise 360 degrees. Through this 3 step process each canister goes sequentially through 3 stages (which we also call "stations" in the following text) to dry materials.

0048. In the first stage the canister is filled with material from the feeder (11). As the canister is being filled the heating process also begins. Heat can be applied by an electrical element or via any heat transfer medium known to one skilled in the art. Temperature can be controlled by a thermostat, and settings can be made easily by simply dialing in the required temperature on the thumbwheels of a controller, or by typing a temperature value in the corresponding field of a computer controlled device.

0049. Once the canister has been heated for the time set it will then index automatically to the next stage, which is equivalent to station (13) of figure 1, where a vacuum is applied. At station 13, the canister is sealed and vacuum is

applied, typically less than 0.1 bar, and preferably less than 10^{-2} bar.

Temperature is also controlled and may be different than in station (12). Moisture is evacuated to ambient air. A controller continuously monitors vacuum level ensuring the vacuum remains sufficient. The time that the canister is held under vacuum is also programmable

0050. After the vacuum cycle is completed the canister indexes again to the material treatment station. Under automatic operation a valve in the bottom of the canister is opened and material then flows from the canister into a material treatment chamber, indicated as 14 in Fig.1 Chamber 14 is sealed to sustain positive pressure, preferably from 0.1 to 15 bar, and filled with gas at a given and controlled temperature, pressure, and composition, the gas or gases being fed in through manifold 15.

0051. The exposure of the material in (14) lasts for a specific programmed time, after which it can be submitted to the exposure of the same or a second gas, under another set of specific temperature, time and pressure conditions. Following one or more exposures to gas, the material is released to the next step. In this next step the treated pellets are either stored in sealed bags for later use in a molding operation which will no longer require the presence of the drying/treatment equipment described above, or they are drawn by a feeder, for instance a vacuum loader or a starve-feeder screw device or any other feeding device known to the industry (all represented by 16 in Fig.1) to the process machine, represented by 17 in Fig.1. At the end of the cycle time the canister will index back to Stage 1.

0052. In a further embodiment of the present invention, the chamber 14 is pressurized with a first gas, up to a required partial pressure and with another diluent gas to the total final pressure. This embodiment is particularly appropriate when the starting resin to be treated by the present invention has been disentangled. For example, typically, when the starting resin is a virgin resin, with no prior disentanglement pre-treatment, station 14 must be pressurized to higher pressures in order to induce significant changes in the future behavior of the pellets. Even if the starting resin had been disentangled, the kinetics of the

treatment will be faster at higher pressures, and pressurizing chamber 14 above atmospheric pressure might be beneficial to the kinetics of the treatment.

0053. In another embodiment of the invention, the pressure of the gas during the treatment in chamber 14, might be either maintained constant during the treatment, or varied according to a specific program, which can include vibratory or pulsatory changes in pressure. The program specifics would depend on the benefits obtained by testing empirically the effect of each process parameter. For example the effect of a fluctuation in pressure amplitude or frequency, on the diffusion of the gas into the free volume of the pellets.

0054. In a preferred embodiment of the invention, the process is controlled by a system with a very simple to use operator interface, and preferably microprocessor based. For example, the dryer would be operated by simply setting the proper temperature and cycle time on the thumbwheels located to the right. The display will indicate temperature and elapsed cycle time or, alternatively, temperature and vacuum level. The controller monitors alarm conditions to ensure proper performance. As an aid to monitoring dryer performance and documenting operation a printer port is provided on the controller. A printed output of dryer operation may be obtained for each drying cycle.

0055. An embodiment of the manifold (15) is shown in more detail in figure 2, in which parts (141), (142), (143) are conduits connecting to gas tanks (145) filled with the permeant, which can be a pure gas, a mix of gases and/or vapors, an aerosol, a fluidized bed, a liquified_gas blended with some chemicals which vaporizes passing through injector nozzles (ultrasonic or otherwise), etc., and (144) are servo-valves, electronically controlled, connected to pressure regulators. The gas tanks could also be replaced by gas generators, such as N2 generators, capable of transforming regular air, sucked in from the ambient atmosphere, into pressurized and purified dry nitrogen. Although three sets of gas tanks and conduits are shown in figure 2, it is to be understood that as many should be present as are needed for the particular polymer plus permeant system that is being treated.

0056. In another embodiment of the invention, one or more of the gas tanks could be an inert gas that acts as a carrier for some other permeant. For example in figure 2 is shown a chamber (146) integral with the conduit (143) into which can be sprayed at a controlled flow rate an aerosol, fine mist, or dust, that is to be carried into the manifold (15).

0057. Figure 3 shows an example of an embodiment of a configuration of a combined vacuum oven and dosing chamber of the invention (25), with vacuum setting and temperature both selectable, in which valves (23) open or close depending on whether the operator is setting up the vacuum connection to the vacuum pump, or inserting a gas A, or several gases A, B etc. Item (24) comprises an automatic feed mechanism with a flow controller, when the chamber is part of a continuous process, or a passageway to the manifold 22, in case of a batch process. The manifold comprises connections to the vacuum side, with 29 comprising a diffusion pump capable of going down to 10^{-2} bar and preferably 10^{-4} bar. A and B comprise two sources of gas with permeant, which can be activated independently.

0058. Item (26) comprises the material to be dried and treated according to the invention. Item (27) is the schematic for an electronically closing/opening valve gate which, at any programmed time, lets material (26) flow to chamber (28). Item (28) comprises either an area for the treated pellets to drop down to a sealed bag, or it is a compartment filled with a fluid containing a permeant that is able to penetrate inside the dried polymer when the pellets drop into it through opening of gate (27). In this embodiment, new material can be fed through a passage through (22) and (24) and a vacuum can be drawn by opening a valve (23) to the vacuum side. At the end of vacuum drying, either the gas A and/or B are activated, then followed by opening of valve gate (27), or an inert gas treatment is supplied to A alone (say pure N₂) to return the chamber pressure to atmospheric pressure. (27) is then opened and the pellets are immersed into a static fluid resting at a certain temperature in (28). After a specific and controlled time, the soaked pellets are separated from the liquid, which is released from the

chamber (28), and the pellets are carried away to either a bagging station, or for further treatment before they are bagged.

0059. One skilled in the art would know how to vary the sequence of events described above, but still not vary from the spirit of the present invention. For instance, heaters for the vacuum oven could be replaced by RF heaters, or any dielectric means capable of rapidly raising the temperature of the plastic during the drying stage. Other means and types of vacuum pumps for obtaining a sufficient vacuum could be applied to the chamber in order to obtain a sufficient vacuum to operate the process. Similarly the invention is not to be construed to being limited to only two additives A and B.

0060. The process of the invention can be scaled to fit in line with a polymer producing reactor. An example of this embodiment is shown schematically in figure 4. A reactor (31) feeds through a conduit (32) and flange (33), which can be a hopper, an extruder plus disentanglement unit (34) with polymer, which is pelletized in (35) and then conveyed to a series of operations (12, 13, 14, 15 and 16) that correspond to the items of the same number in figure 1, described above. Treated polymer is then fed to a bagging station (36) for storage and future processing. Alternatively the pellets from 16 can be fed to an on-line processing unit, for example extrusion, injection molding, blow molding or other processing operation known to one skilled in the art.

0061. The equipment represented in figure 4 can be scaled to be attached at the end of a resin manufacturer's reactor and produce large scale quantity of "ready to use" treated resin, according to the claims of the present invention.

0062. The possible embodiments of the invention are not intended to be limited by the description above of figures 1 to 4. For example, the drying and permeation steps can be carried out in an extruder, instead of in the feed mechanism to an extruder. An example of a combination extruder plus dryer is that provided by the French Oil Mill Machinery Company (Piqua, OH) under the part number "R-176 extruder – dryer". The R-176 uses a jacketed main barrel to carry a heat transfer fluid through to up to three separate control zones. In a

modification of this machine that will be obvious to one skilled in the art, the zones can be used for drying and permeation of the pellets, before melting of the polymer takes place in a final zone.

0063. All steps of the process can then be carried out sequentially on line in a conveying device, a modified extruder, which has sealed compartments. For example, in one embodiment could describe, the angle of the helicoidal flight flange could be adjustable from tilted (to convey forward) to straight perpendicular (to hold the pellets inside stationary at a given spot, to effect treatment of a certain kind for a certain time (like vacuum or heating or both, or permeation by a gas or a liquid). A software program would therefore direct the motion of the pellets from one station to the next, by triggering by a certain mechanism the change of the helicoidal angle, from straight to tilted, Or, if the conveying system is vertical, the screw can be rotating with no descending motion, only a stirring effect would be perceived, until the sealed trap separating sections is opened, which would release to the next station, a given quantity of pellets ready for the next treatment.

0064. The mechanism for heating the polymer need not be indirect, via a heat transfer medium, and radio frequency or microwave electromagnetic radiation could be used to heat the polymer directly.

Example

0065. In the following example, molecular weight measurements are performed using a Waters 150CV+ automated gel permeation chromatography (GPC) apparatus (Waters Inc., Milford, MA). For the polycarbonate measurement, tetrahydrofuran (THF) is used as solvent, and a refractive index (RI) detector.

Example 5

0066. This example shows the ability of the invention to create disentanglement in a resin without the use of the equipment and process of the patents (Ibar) described previously.

0067. Virgin polycarbonate pellets were dried at 65°C for 17 hours and then treated with a gas mixture at 65° C and a pressure of 2 bar. The gas mixture contained methanol at a partial pressure of 0.75 bar, applied first, and nitrogen at

a partial pressure for 1.25 bar. Melt index was determined at 300° C and the % chain scission was determined to be 17% and degree of disentanglement to be 77.5%.

Other Embodiments

0068. In the embodiments of the examples described above the permeant is introduced in one stage to the polymer. However, in alternative embodiments, the permeant is introduced in two stages. For example in a first stage, the permeant is introduced at a pressure in the preferred range of range of 0.1 bar to 20 bar, and in a second stage at a different pressure or the same pressure than the first stage. For example, in one embodiment the second stage is at a lower pressure than the first stage. In another embodiment, the second stage is at a higher pressure than the first stage. The invention is not to be construed as limited to these examples, however, and one skilled in the art will be able to perceive of alternative ways of introducing permeant to polymer that are to be considered as falling within the scope of the present invention.

0069. In yet another embodiment, at one stage the permeant contains a chemical component that is capable of breaking polymer chains, such as for example water or methyl alcohol in the case of polymers made by condensation reactions, and in a second stage the permeant contains a polymer chain building reagent, such as a cross linking agent or branching agent, or cyclic monomers, such as cyclic butylene terephthalate (CBT), capable of very fast ring opening and local chain growth.

0070. The conditions under which the process of the invention is operated, such as pressures, temperatures, concentrations, and reaction times, are determined as a function of the objectives that the operator or polymer fabricator wishes to accomplish. The present invention gives the fabricator the possibility to tailor the properties and in particular the processability of the resin at will.

0071. The invention is also not intended to be limited as to the nature of the permeants or polymers that can be processed thereby, and any polymeric molecule that can be disentangled can be used in the invention. For example; ethylene propylene copolymer, high-density polyethylene, high-impact polystyrene,

low-density polyethylene, polyamide, polyacrylic acid, polyamide-imide, polyacrylonitrile, polyarylsulfone, polybutylene, polybutadiene acrylonitrile, polybutadiene styrene, polybutadiene terephthalate, polycarbonate, polycaprolactone, polyethylene, polyethyl acrylate, polyetheredierketone, polyethylene sulfone, polyethylene terephthalate, polyethylene terephthalate glycol, polyimide, polyisobutylene, polymethyl acrylate, polymethyl ethyl acrylate, polymethyl methacrylate, polyoxymethylene (polyacetal), polyphenylene ether, polyphenylene oxide, polyphenylene sulfide, polypropylene terephthalate, polystyrene, polytetrafluoroethylene, polyurethane, polyvinyl alcohol, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polyvinylidene fluoride, polyvinyl methyl ether, polyvinyl methyl ketone, styrene butadiene, styrene butadiene rubber, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cellulose nitrate, chlorinated polyethylene, chlorotrifluoroethylene, ethylene acrylic acid, ethylene butyl acrylate, ethyl cellulose, and polymers and copolymers of acrylonitrile butadiene acrylate, acrylonitrile butadiene styrene, acrylonitrile, chlorinated PE and styrene, acrylonitrile methyl methacrylate, acrylonitrile, acrylonitrile styrene, acrylonitrile, butadiene acrylonitrile, ethylene propylene diene monomer, and blends or copolymers of the preceding.